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INVESTIGATION OF INTEGRALLY COMPOSED VARIABLE ENERGY GAP PHOTOVOLTAIC SOLAR ENERGY CONVERTER



THE EAGLE-PICHER RESEARCH LABORATORIES

Chemicals & Metals Division

Miami, Oklahoma

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Covering the Period -

February 9, 1961 - July 10, 1961

Report Date : July 10, 1961

"INVESTIGATION OF INTEGRALLY COMPOSED VARIABLE ENERGY GAP
PHOTOVOLTAIC SOLAR ENERGY CONVERTER"

ARPA Order Number 80-61

Date of Contract: February 9, 1961

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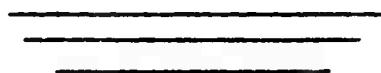


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80-61 through the U.S. Army Signal Research and Develop-
ment Laboratory.

I. PURPOSE

The general objective of this work is to fabricate and study an integrally composed variable gap solar cell and determine the feasibility of improving the photovoltaic properties of solar cells through the use of the variable gap principle. Specific objectives are to - (1) increase the conversion efficiency, and (2) improve the temperature coefficient of conversion efficiency, V_{OC} and I_{SC} . The variable gap solar cell under study is fabricated from an alloy of two III-V compounds - GaAs and GaP - in which the cell surface is composed principally of GaP forming a 'window' of higher band gap than the gallium arsenide portion of the cell. A specific objective is to determine the feasibility of using such a window of higher band gap to achieve higher collection efficiency and lower the sheet resistance.

II. ABSTRACT

Gallium phosphide as a discrete phase was produced by the diffusion of phosphorus into gallium arsenide. Diffusion of phosphorus into gallium arsenide powder of 5.2 microns radius under a phosphorus vapor pressure of 20 atmospheres resulted in the formation of a discrete phase of gallium phosphide. Concentration of discrete phase GaP in the diffused powder was determined by x-ray studies to be 82.3 percent, with GaAs determined as 17.7 percent. An advantage of variable gap GaP-GaAs cells over single gap GaAs cells is indicated in elevated temperature characteristics, particularly in I_{sc} change. Zinc diffusion by the open tube hydrogen technique offers excellent junction depth control and expedites fabrication over the sealed ampoule techniques. Reliable ohmic contacts to 'p' type GaAs can be produced by sputtering with platinum followed by coating with solder or baking on silver paste. It is indicated that non-homogeneity in gallium arsenide single crystals can have a serious negative influence on diode characteristics and conversion efficiencies of solar cells made therefrom.

III. PUBLICATIONS, CONFERENCES, & REPORTS

Conferences.

A conference was held at Eagle-Picher Research Laboratories, on February 14, 15, and 16, 1961, with Mr. L.Schwartz of Evans Laboratories, Fort Monmouth, and Mr. W.E.Medcalf and Louis E. Stone of this laboratory. The subject of the conference was the direction and emphasis of the projected investigation. Methods of fabrication, testing, and evaluation were discussed and an outline of future work agreed upon. The conference was useful and informative.

A second conference was held on March 30, 1961 at Evans Laboratories, Fort Monmouth, New Jersey. Present were Mr. Cherry, Mr. J. Mandelkorn, Mr. L.Schwartz, Mr. J.Kesperis, and Mr. Louis E.Stone. The subject of the conference included current progress of studies, formulation of testing procedures with regard to elevated temperature tests, integrated red response of the variable gap cell, and diode testing techniques. At this conference ten sample specimens of GaAs wafers diffused in varying degree with phosphorus were delivered. The conference was useful and lent direction to further efforts.

The Annual Power Sources Conference was held at Atlantic City, New Jersey, on May 9, 10, and 11. It was attended by Mr. Stone of this laboratory. Following the Power Sources Conference, a private conference was scheduled and held at Evans Laboratories on May 12. At this conference, Mr. Mandelkorn mentioned that a discrete phase of GaP had been identified on at least one of the sample specimens delivered March 29 - corroborating our own x-ray determination of a previous date. Further specimens (4) of cells were delivered at this time.

Reports: Monthly letter-type progress reports have been submitted on or before the 4th. day of each month, beginning April 4, 1961.

IV. FACTUAL DATA

A. Introduction:

The theoretical basis for the research performed on this contract has been discussed in detail in previous reports.⁽¹⁾ Briefly the integrally composed GaAs-GaP cell would have a surface composed principally of gallium phosphide, with the GaP content diminishing below the surface. The higher band gap of the GaP layer should allow transmission of lower energy photons nearer the junction, improving collection of the hole electron pairs formed, hence increasing the efficiency. The higher band gap material should also enhance the high temperature performance over single gap cells.

The practical object of the work, as defined in the March 30 conference at Fort Monmouth, is to "demonstrate advantageous characteristics of such a cell, such as better temperature coefficients of V_{oc} , I_{sc} , or efficiency for special applications when the state of the art material wise makes GaAs competitive with present materials, and to demonstrate the feasibility of using such a "window" made by introducing a material of higher band gap to achieve higher collection efficiencies and lower sheet resistance".

B. Approach to the Problem:

The approach to the problem is as follows:

1. Study of gallium arsenide crystals, to improve starting material in purity, stoichiometry and crystalline perfection.
2. Study of the fabrication of variable gap cells to achieve the desired structure of the variable gap cell, and, secondly, the study of the structure of single gap cells as a standard for comparison. This

encompasses many factors, such as -

- (a). Techniques of forming p-n junctions in both types of cells, with particular emphasis on control of depth, density of dopant, and homogeneity of diffused layer.
- (b). Diffusion of phosphorus to produce the compound gallium phosphide, instead of diffusion as an interstitial impurity.
- (c). Identification of the gallium phosphide concentration and depth and techniques of controlling them.
- (d). Electroding and contacting the cells with emphasis on ohmicity and low resistance as well as temperature stability.

3. Evaluation of cells.

The evaluation and comparison of the cells is considered of prime significance. Parameters which could indicate improved collection and better temperature coefficients include:

- (a). Conversion efficiency.
- (b). Spectral response.
- (c). V_{oc} temperature coefficient.
- (d). I_{sc} temperature coefficient.
- (e). Eff_{mp} temperature coefficient.
- (f). Diode characteristics as a function of temperature.

Other parameters considered significant include -

- (a). Dark diode characteristics.
- (b). Sheet resistance of surface.
- (c). Carrier concentration in the diffused area.
- (d). Electrode contact resistance.

4. Demonstration of the Window Effect of the Higher Band Gap Material.

The optical absorption of GaAs is known to be high, hence if the removal of the GaP layer can be demonstrated to cause little change in absorption of wavelength absorbed by the GaAs, it would substantiate, if not prove, the "window" effect of the higher band gap material. A relatively simple technique to obtain such data is considered in this report.

5. Evaluation of Material Parameters as to Cell Performance.

It is considered important to establish the effect of the following on temperature and photo parameters:

- (a). Resistivity.
- (b). Mobility.
- (c). Lifetime of minority carriers.
- (d). Crystal orientation.
- (e). Any difference between the gallium or arsenic "face" of the crystal.

C. Fabrication:

1. Materials.

The gallium arsenide used consisted of material from the following sources:

- (a). The Eagle-Picher Company.
- (b). Monsanto Chemical Company.
- (c). The Texas Instrument Company.

The crystals were of three types - Czochralski grown crystals, gradient freeze crystals, and float zoned crystals. Table I illustrates typical material data.

TABLE I.
Typical Material Parameters of Starting Material.

Type Material	Crystal Structure	Resist- ivity.	Mobility $\text{cm}^2/\text{V/sec.}$	Cartier Conc. Atoms/cc
V-294.	Gradient Freeze,	Single	.057	2.54×10^{16}
G-94	Gradient Freeze,	Single	.002	4410×10^{17}
G-101	Gradient Freeze,	Single	.006	2233×10^{17}
G-125	Gradient Freeze,	Twinned	.0038	2520×10^{17}
V-252	Czochralski,	Single	.013	3030×10^{17}
T-121	Czochralski,	Single	.104	3300×10^{16}
V-297	Float Zoned,	Single	.078	2.4×10^{16}

2. Sequence of Fabrication.

Listed below are the routine steps in fabrication of both single gap and variable gap cells. Some steps will be discussed individually.

Cell Fabrication Step Sequence

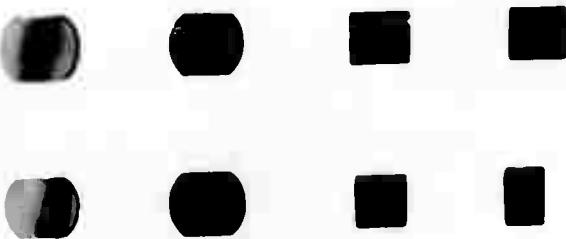
	<u>Variable Gap</u>	<u>Single Gap</u>
(a). Dice Material to appropriate size,	X	X
(b). Lap with 600-grit compound to clean off saw debris,X		X
(c). Polish, ending with Linde "B" Compound,	X	X
(d). Clean 10 min. in 100°C concentrated HI acid,	X	X
(e). Thoroughly rinse, ending with de-ionized water, blot dry,	X	X
(f). Seal off in flushed, evacuated ampoule with appropriate charge of high purity phosphorus and diffuse,	X	
(g). Clean in 100°C Concentrated HI acid,	X	
(h). Thoroughly rinse, blot dry,	X	
(i). Diffuse zinc to form junction,	X	X
(j). Mask surface with Krylon, lap bottom surface thoroughly with 3-F Compound,	X	X
(k). Plate (electrically) nickel on bottom surface,	X	X
(l). Lap edges with 3-F Compound,	X	X
(m). Dissolve Krylon with 3 baths acetone, ultrasonically, and rinse	X	X
(n). Clean 2 minutes 100°C HI acid, rinse thoroughly, blot dry,	X	X
(o). Mask all surfaces, sputter platinum collector on top,	X	X
(p). Apply either solder, or baked on silver paste to platinum collector,	X	X
(q). Cell ready for evaluation.		

Surface preparation became important in reproducibly forming shallow p-n junctions. Two techniques have been used, chemically polishing with 1-HF: 3-HNO₃:1-H₂O, and lap-polishing followed by cleaning as indicated above. Diffusion is rapid into either, but when initial junction depths of 1-micron are intended, etch pits and surface imperfections produced by chemically polishing prove detrimental to V_{OC} and cell efficiency. This is especially true of the open tube hydrogen diffusion of zinc. The latter method is therefore preferred. The use of concentrated HI acid as a clesning agent has proved useful in removing any films, oxide or otherwise, and does not attack GaAs. A study indicated zero weight loss of a normal size GaAs wafer after 24 hours immersion. Nickel contacts are not attacked to any significant degree, although any of the more active metals are readily taken in solution. The etching therefore removes any excess zinc which may condense on the surfaces. Finished cells may be cleaned for periods of minutes with no deterioration of photo parameters. Indeed, it is advantageous as a "clean up" treatment to reduce edge leakage. Cleaning and rinsing is done gently, ultrasonically, and always ends with de-ionized water - blotting dry to prevent any residue.

Figure 1 illustrates polished, clean wafers ready for fabrication, and Figure 2 illustrates completed cells of both types.

3. Contacting:

Initially, contacting the active "p" surface was done using silver paste. Proposed temperature studies at elevated temperatures, especially those involving cell efficiencies, pointed up the need for more stable contacts.



POLISHED GALLIUM ARSENIDE WAFERS

Figure 1. Polished Solar Cell Blanks Ready for Diffusion.

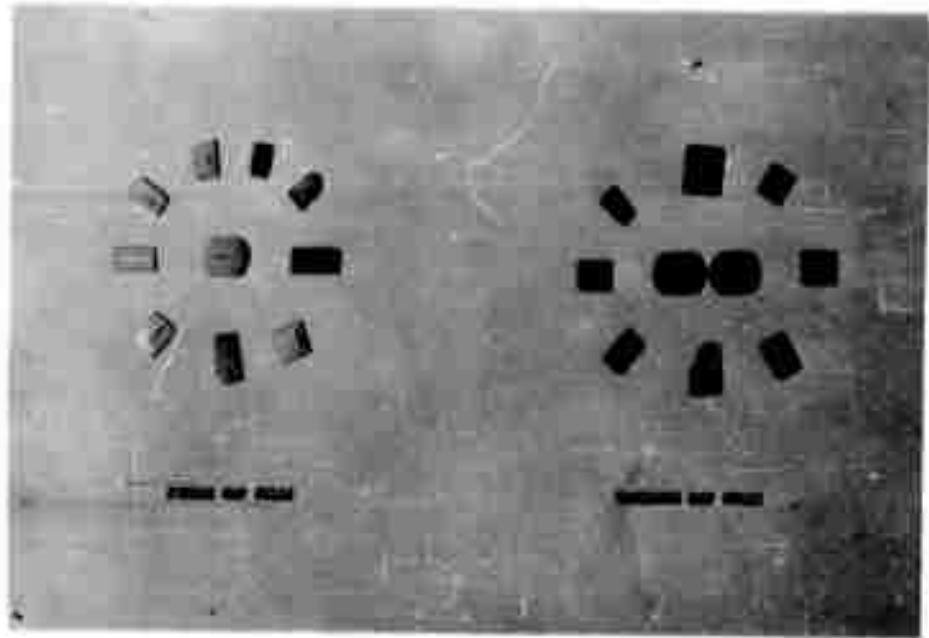


Figure 2. Completed Solar Cells

Present practice is to sputter a platinum contact stripe, followed by either (a) solder coating using Divco #335 Flux, or (b) coating with silver paste, followed by a 100°C - 1 hour baking cycle.

Dark diode data indicate (a) to be best, with (b) also excellent, and allowing subsequent removal when desirable, without damaging the platinum. Attempts to remove solder coated contacts always damage the platinum layer.

D. Phosphorus Diffusion.

In variable gap cells phosphorus is diffused first, followed by diffusion of zinc, due to the mobility of the zinc dopant at temperatures above 500°C. When a cell having a zinc diffused junction is subjected to the phosphorus diffusion heat cycle, the gradient at the junction becomes less sharp, seriously deteriorating cell performance.

The formation of GaP by solid state diffusion of phosphorus has been one of the more difficult problems in this work. The diffusion constants for phosphorus in gallium arsenide are known to be low - of the order of 10^{13} cm² per second at 700°C.⁽²⁾ The formation rate of GaP would appear to be of the same order. The presence of single phase GaP formed during diffusion of phosphorus under 10 atmospheres pressure at 1000°C for 20 hours was determined early in the first work in this laboratory by DeBye-Scherrer X-ray powder studies. More recently, it's presence was determined in an x-ray study carried out in the laboratory of another company - using a phosphorus diffused wafer prepared by us and delivered to Mr. Cherry at Fort Monmouth on March 29, 1961.

The specific depth and concentration of the GaP has been difficult

to establish. Some progress has been made recently. The x-ray powder technique has suffered the handicap of inherent low total concentration when the GaP is removed from the surface of a wafer, since a minimum of at least several microns of material must be removed from the wafer. In another approach to the problem, some GaAs was ground to a fine powder by mortar and pestle, under kerosene to prevent oxidation. It was carefully washed by decanting in acetone many times, then in alcohol several times, finally in de-ionized water three times, and dried carefully at 95°C in an inert atmosphere. A sample of the powder, undiffused, was analyzed for particle size, since micron range screening was not available. Particle sizes are indicated below in Table II.

TABLE II.
Particle Size Distribution of GaAs Powder

Size	Percent of Total	Size	Percent of Total
0 - .015 Micron	.3%	1. - 2. Micron	9.2%
.015- .03 "	.3%	2. - 4. "	18.8%
.03 - .06 "	.3%	4. - 8. "	32.2%
.06 - .125 "	.7%	8. - 16 "	23.4%
.125 - .25 "	1.3%	16 - 22 "	5.9%
.25 - .5 "	2.3%	22 Micron to #325 Mesh	.9%
.5 - 1. "	4.5%	Greater than 325 Mesh	.9%

Median Particle Size = 5.2 microns radius.

The powder was then diffused at 20 atmospheres phosphorus pressure at 900°C for 50 hours. The powder sample was used for DeBye-Scherrer X-ray

determination. Table III indicates positive identification of single phase GaP. Concentration was determined to be 82.3 percent GaP, 17.7 percent GaAs.

TABLE III.

Lattice Spacings Providing Evidence of the Presence of a Discrete Phase of Gallium Phosphide as a Result of Diffusion of Phosphorus into Gallium Arsenide under a Pressure of 20 Atmospheres.

Calculated			Measured		Calculated			
<u>h</u>	<u>k</u>	<u>l</u>	Sample in Air M6107 AA	Sample in Kerosene M6107 AB	<u>h</u>	<u>k</u>	<u>l</u>	As_2O_3
111	3.1468	3.3640	3.2441 3.158 2.148	3.165 2.735 -	111	6.394		
220	1.9270	1.9980	1.959 1.940 1.667	1.940	222*	3.1968		
311	1.6434	1.7046	1.654	1.655	400	2.7685		
			-	-	331	2.5405		
					440	1.9576		
					622	1.6695		
					711	1.5507		
400	1.3626	1.4133	1.371	1.372				
331	1.2504	1.2970	1.258	1.258				
422	1.1126	1.1540	1.119	1.120				
513-333	1.0489	1.0880	1.054	1.055				
440	.96352	.99939	.96937-1 .97010-1 .92703-1	.96937-1 ----- .92790-1				
531	.92130	.95560	.92713-2 .86726-1	.92908-2 .86758-1				
620	.86180	.89388	.86695-2 .83655-1	.86779-2 .83655-1				
533	.83119	.86214	.83648-2 .79189-1	.83643-2 .79189-1				
444	.78671	.816000	.79168-2	.79125-2				
A_0	5.4505	5.5634	5.487	5.485				11.074

*Strongest line

Mean $A_0 = 5.468 \text{ \AA}^\circ$

Approximate Composition 82.3% GaP
17.7% GaAs

The very definite line in the 2.74 Å° region of both sample patterns is not readily explained. It is close to the position of the forbidden 200 line of the gallium compounds. It is not in close agreement with the arsenic-trioxide line at about 2.77 Å°. Perhaps the ordering of the GaAs-P solid solution permits this plane to diffract and one might expect the intensity of this line to vary with method of preparation and in particular the thermal history of the sample. The absence of some of the strong As_2O_3 lines is a strong argument for it's absence as a discrete phase.

Using median particle radius of 5.2 microns, simple mathematical treatment produces a median depth of 2+ microns of material converted to GaP. It is recognized such treatment lacks precise accuracy, especially with regard to non-uniform particle size. Future determination would include more uniform particle sizes.

Phosphorus diffusion constants of 1×10^{-13} at 700°C ⁽²⁾ and 4.3×10^{-9} at 1100°C were noted in the literature. Using a median value for 900°C of $2 \times 10^{-11} \text{ cm}^2/\text{sec.}$, one calculates that 50 hours diffusion would produce a depth of only .036 microns. Obviously there exists a wide discrepancy. It is considered that the diffusion process would be accelerated due to the high pressure present, and secondly, the diffusion soon becomes that of phosphorus through GaP as the surface layers become predominately GaP. This study is only partially complete, yet it appears promising in establishing a method of predicting GaP depth.

Mention has been made of high (10-20 atmospheres) phosphorus pressure. Pressures of at least 10 atmospheres are considered vital to the formation of single phase GaP. An explosion hazard exists, but may be avoided

by using quartz ampoules whose wall thickness/diameter ratio is no less than 1:4. Careful sealing is required to prevent thinning of the walls. After diffusion, the ampoule is pulled to the end of the hot zone. Slow cooling condenses the phosphorus at the end of the ampoule, keeping cell surfaces clean of any elemental phosphorus deposit. Figure 3 illustrates an ampoule ready for diffusion, showing placement of phosphorus, tantalum getterer, wafers, etc. Figure 4 illustrates the same ampoule after diffusion and indicates the selective condensation of phosphorus at the end.

In the course of studying phosphorus diffusion at low pressures, a shallow p-n junction, with appreciable photo output was noted. Brief investigation indicated the junction was formed when (a) pressure of ambient was less than 8 atmospheres, especially in vacuum, and (b) when temperature of treatment exceeded 600°C, especially around 800°C for periods of 2 hours, and (c) when no other known impurities were present. The junctions typically were about 1-micron deep, produced V_{oc} up to .73 volts, I_{sc} of up to 9 ma/cm², Eff_{mp} of up to 2 percent. Surface 4-probe resistivity ranged rather high, 400 to 1000 ohms/square. It was determined the p-n junction was not formed when phosphorus pressure was increased to 8 atmospheres or more. Consideration of all facts indicates that the junction formed as the result of loss of arsenic from the surface, producing a "p" type layer of high sheet resistance. It is an interesting effect, but poses no special difficulty to fabrication of cells.

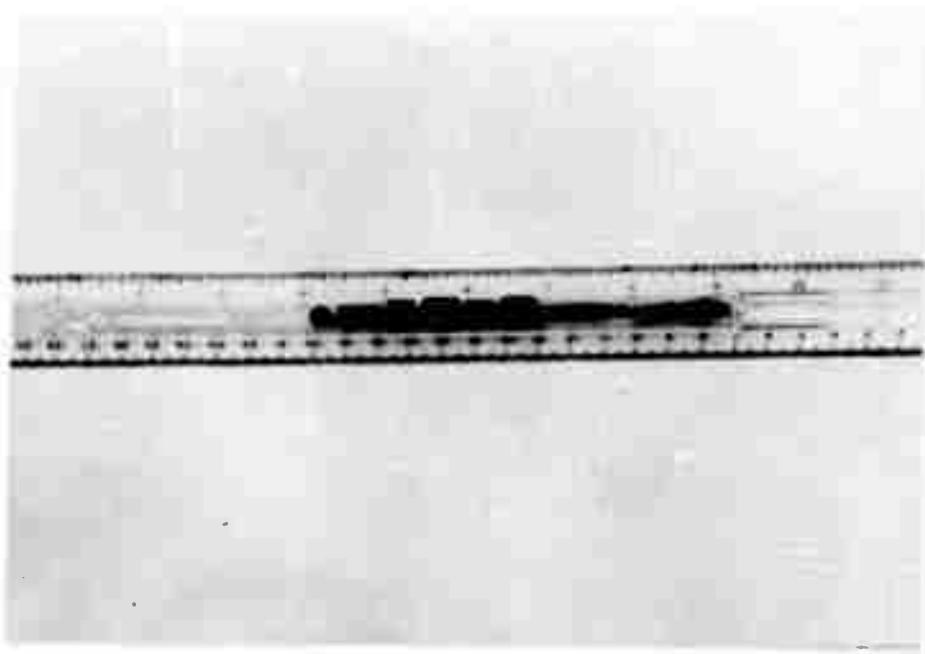


Figure 3. Evacuated Ampoule, Phosphorus, Tantalum Getterer and Wafers Before Diffusion.

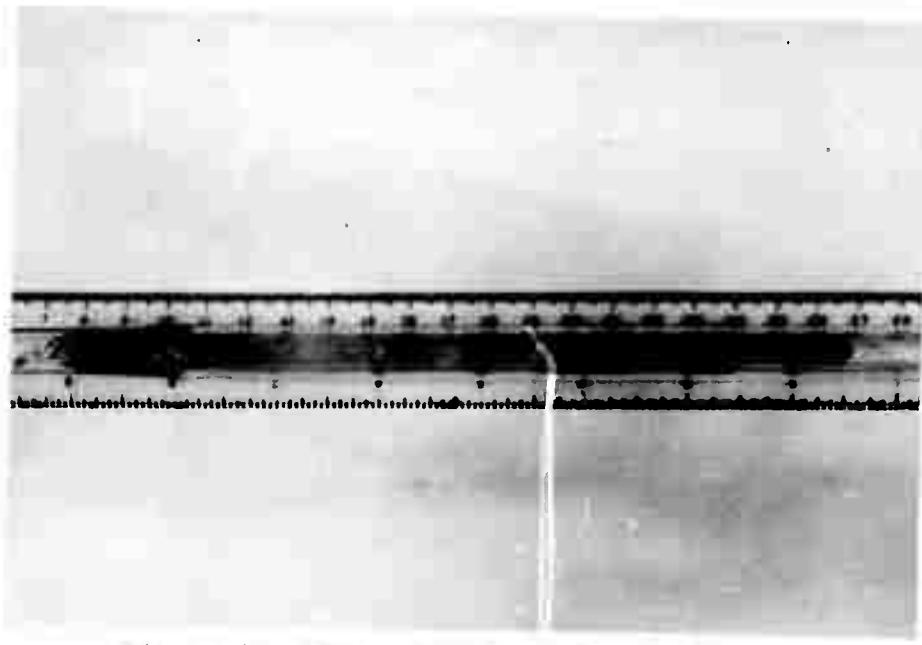


Figure 4. Same Ampoule After Diffusion.



**Figure 5. GaP Crystals on Surface of Variable Gap Cell.
(1000 x magnification)**

During evacuation of the ampoules, vacuum pressure on occasion has lifted fine particles of phosphorus which fell on the surface of the wafers. Subsequent diffusion resulted in spots where each particle lay. Microscopic examination indicates these spots to be GaP crystals. Figure 5 illustrates such an area of GaP crystals. Such spots produce photovoltaic output; in the interest of homogeneous surfaces however, they may be prevented by using only large grain size phosphorus, and gently initiating vacuum pumping.

E. Zinc Diffusion:

The need for precise control of p-n junction depth prompted a study of zinc diffusion as a function of temperature and time, using the evacuated ampoule technique. Zinc charge was kept constant, of the order of 150 micrograms. Accuracy of this charge, and ease in handling was enhanced by plating the zinc on 20 inch lengths of molybdenum wire, .020 diameter, weighing the increase, and cutting the plated wire in appropriate lengths. An effective increase in weighing of 20 was thus obtained. Temperatures of interest were below 800°C, junction depths of 1-micron or less were desired. Figure 6 summarizes graphically the results of this study. Optimum appears at 550°C for 10 minutes. The absolute efficiencies shown are low; no special effort was made to select material for high efficiencies in this study.

One factor, significant in producing abrupt gradient junctions, is the method of cooling following the zinc diffusion cycle. Rapid, quench-type cooling produces the sharpest gradient junctions. The evacuated ampoule technique is awkward from the handling and cooling standpoint. Investigation of the previously proposed open tube-hydrogen ambient technique of zinc diffusion proved it to be advantageous, and equally effective. Perfect surface conditions equal to the evacuated ampoule method was maintained using this technique, and no film formation was noted. It is quicker and eliminates an evacuation-sealing operation, hence has become routine in recent work. Table IV illustrates typical diffusion data.

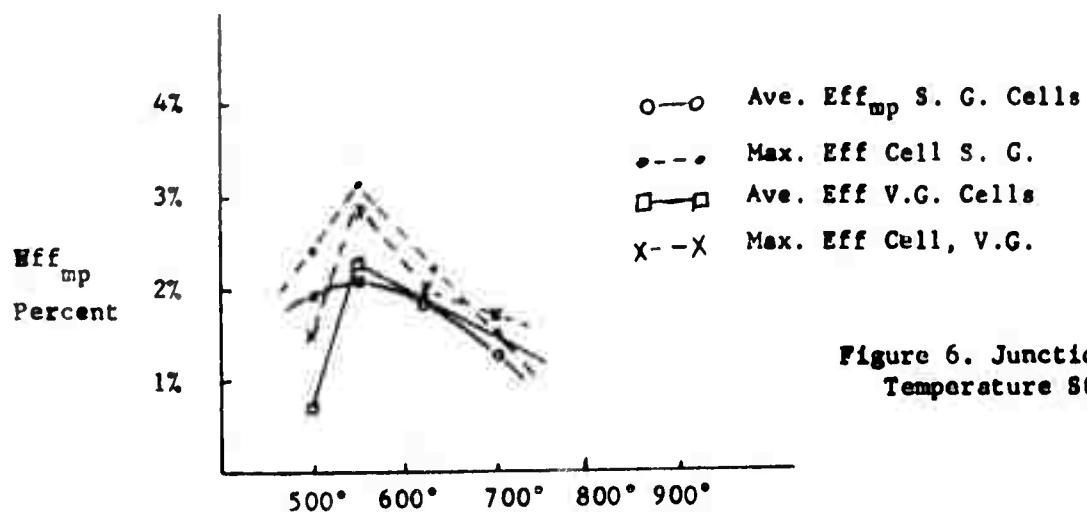
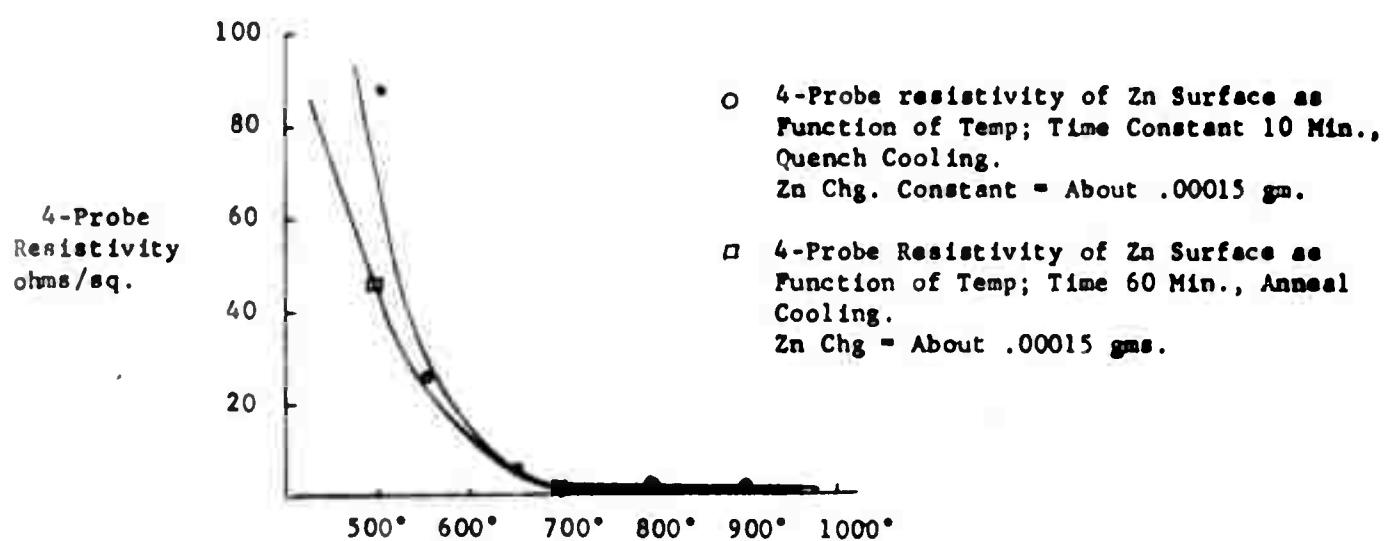
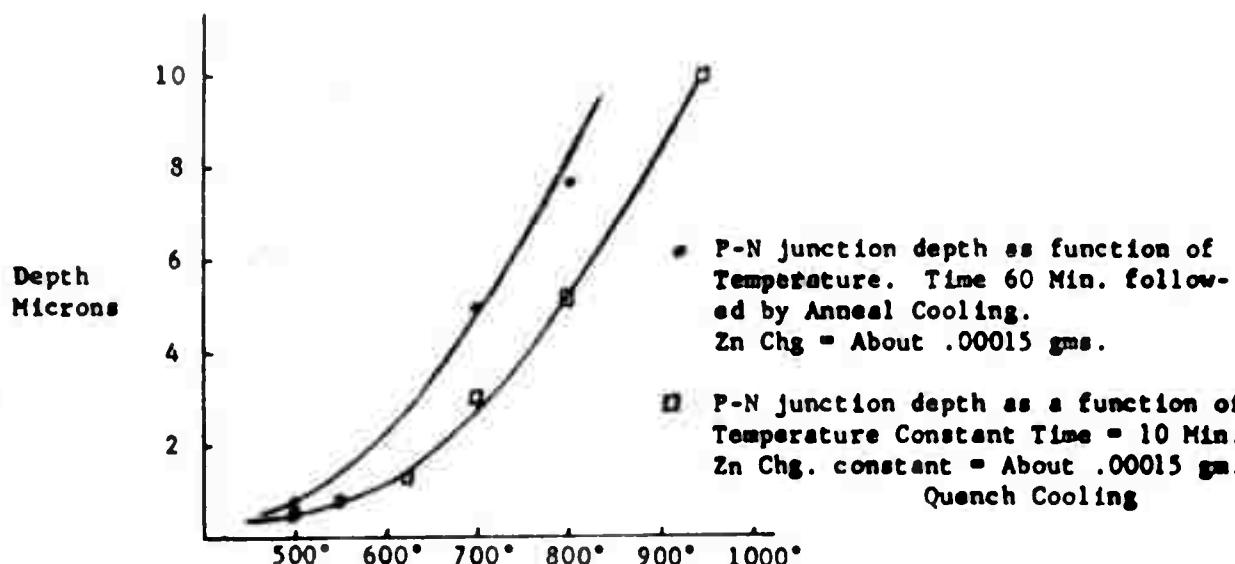


Figure 6. Junction Depth, Temperature Studies.

TABLE IV.

Typical Zinc Diffusion Data Using Open Tube-Hydrogen Ambient Technique.

<u>Temp °C.</u>	<u>Time-Min.</u>	<u>Depth-Microns</u>	<u>Resistivity ohms/sq.</u>
700°C	10 Minutes	3.0+ Microns	1.0 - 2
700°C	5 "	2.0 "	6.0 - 10.
600°C	6 "	1.0 "	10.0 - 20.
600°C	4 "	.5 "	20.0 - 50.

Zinc diffusion carried out in a Hevi-Duty 3-zone furnace, is illustrated by Figure 7. Wafers are placed in a clean quartz boat, with the zinc dopant in each end, distant from the wafers at the center. The boat is held at one end of the tube, at near room temperature, during outgassing and heating of the furnace. With the tube filled with hydrogen, stabilized at the desired temperature, the boat is moved to the center of the hot zone, hydrogen flow reduced to near zero, for the desired time. Figure 8 illustrates the boat in place in the hot zone of the furnace. At the end of this time period, hydrogen flow is increased to "sweep out" vapor, the boat is moved back to the end of the tube, and evaporative cooling reduces the temperature to less than 300°C within 3 minutes. Subsequent slower cooling and purging allows the removal of the cells.

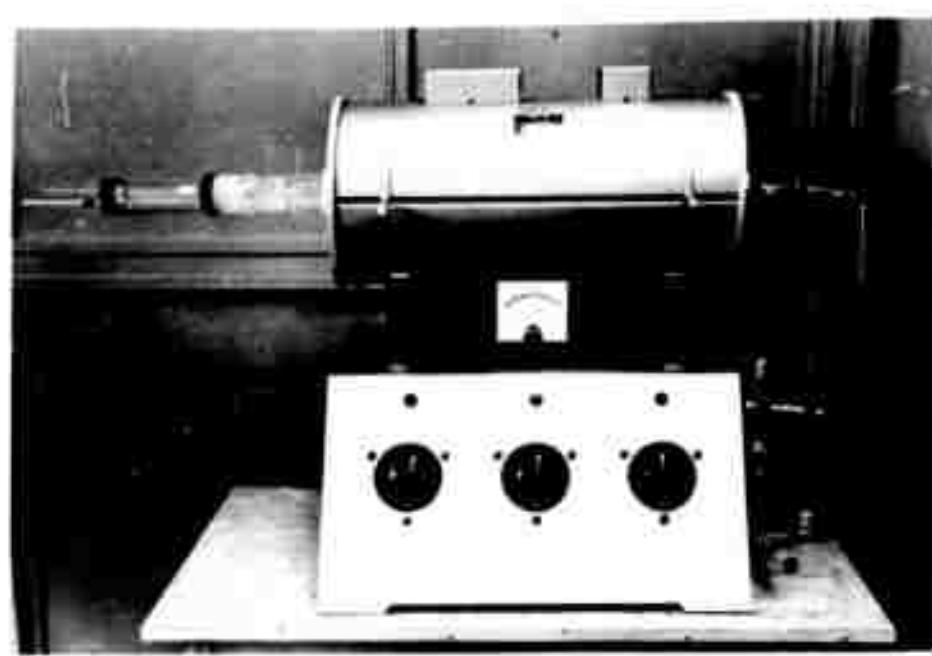


Figure 7. Heavy-Duty 3-zone Furnace for Zinc Diffusion.

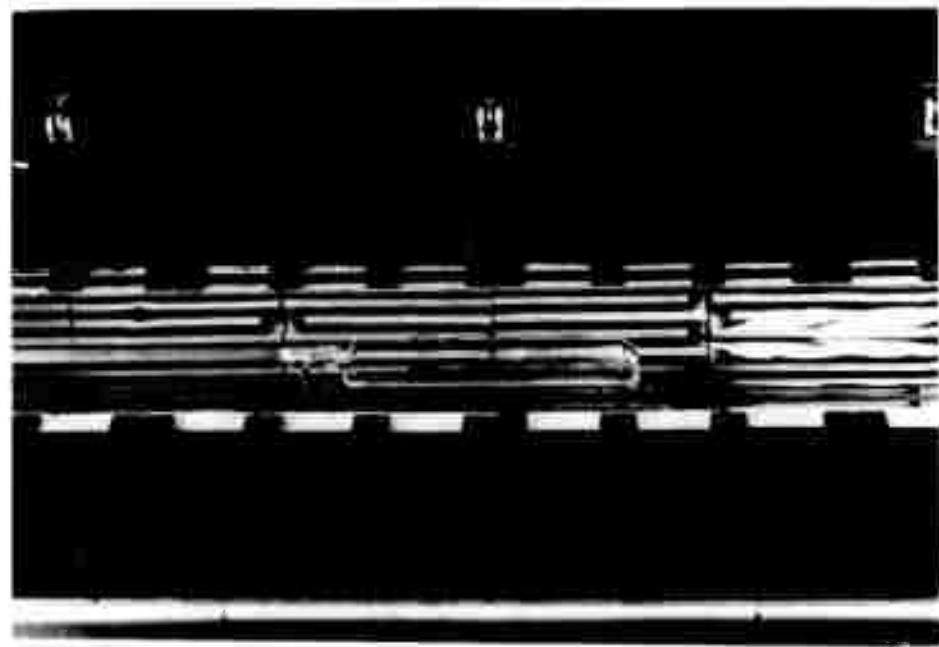


Figure 8. GaAs Wafers and Boat in Place for Zinc Diffusion.

F. Cumulative Studies:

As a coherent part of the principle objective, viz., proving the variable gap principle, long term accumulation of data with respect to efficiency, resistivity, mobility, and other material properties can provide useful information. One additional factor can be included with very little additional effort, i.e., gallium or arsenic "face" identity. The only requirement, identity, is obtained by a simple etching procedure at the material preparation stage. The etchant solution used is 1-HF:2 H₂O₂: 5 H₂O.

Figure 9 and Figure 10 illustrates the appearance of the two faces under 500x magnification.

- (1). Conversion of GaAs to GaP as a function of face identity has not been defined as yet; it's significance will be clarified concurrently with increasing control in formation of the GaP layer thickness.
- (2). Efficiency as a function of face identity - tentatively we can not relate the efficiency to face identity. This also will clarify with accumulated data.
- (3). Efficiency as a function of mobility, resistivity, and lifetime.
Data is being assembled and accumulated with the objective of making possible the specification of the resistivity of material which will give highest efficiency solar cells. Mobility and lifetime, of course, should be the highest available as the state of the art of material growth progresses.
- (4). Material type - comparative data of Czochralski, gradient freeze and float zoned material is also being compiled to allow selection of the best form for solar cell efficiencies. Since only limited amounts have been used, and only very recently, it is considered unwise to make any deductions or comparisons at this time.



Figure 9. Etch Pits Identifying Gallium Face of GaAs.



Figure 10. Etched Surface Identifying Arsenic Face of GaAs.

G. Evaluation:

1. General:

Measurements of efficiency are most accurate when made in sunlight. Intensity values are made using a 50-junction Eppley Pyrheliometer, recently obtained for this purpose. For indoor testing, a source using 5 outdoor photo-flood bulbs was constructed. It proved difficult - if not impossible - to correlate with short circuit currents obtained in sunlight, apparently due to the color temperature of the radiated light. Better results, with close correlation of both I_{sc} and Eff_{mp} to sunlight values, was obtained using one RFL-2 bulb in this source. No water filter is used to absorb infrared, hence cell temperature rises somewhat during measurement. A modification of the cell holder to permit stabilized temperature by circulation of water is under construction.

Short circuit currents are measured as a voltage drop across a precision 1-ohm resistor, using a vacuum tube voltmeter such as Millivac, or Keithley Model 200-B.

Photo parameters at elevated temperatures are measured by placing a cell in a special "jig", in a thermostatically controlled furnace. The jig is illustrated in Figure 11.

The oven, a Blue M Stabil-Therm Model OV-12A, has provisions for-

- (a). Temperature measurement by thermocouple of cell pedestal temperature.
- (b). Ambient temperature measurement by thermometer.
- (c). Cell instrumentation leads.
- (d). Light entry through a 3-inch diameter quartz optically flat window in the top.

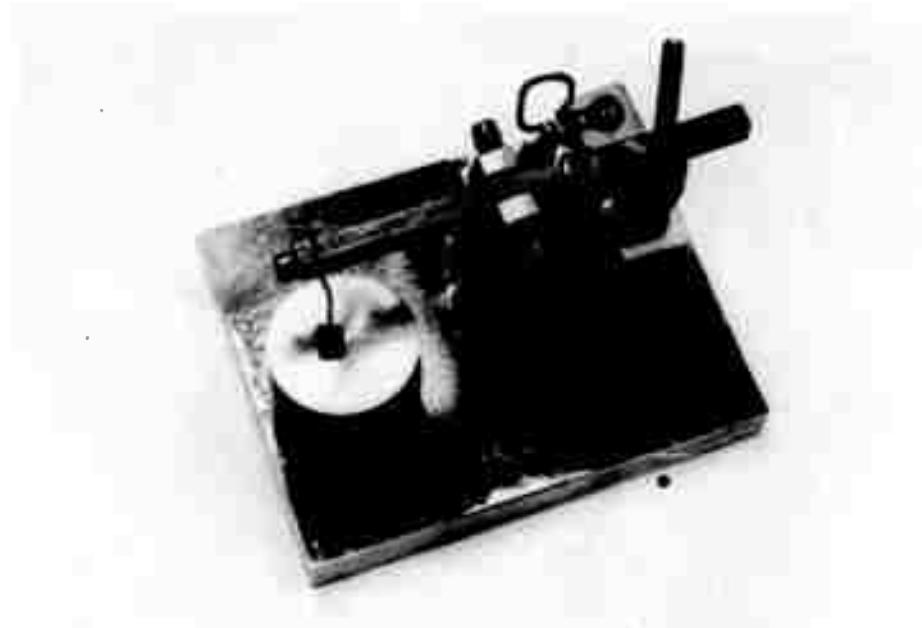


Figure 11. Cell Holder Jig for Temperature Studies.

The base and pedestal are of aluminum, with coinciding surfaces polished to insure good thermal conductivity. The yoke and arm are of mild steel, gold plated to prevent oxidation and rusting. Electrical insulation is obtained from glazed porcelain insulators, tapped and threaded for machine screws. Electrical connections are made with pressure crimped lugs, since the entire assembly must be heated to 200°C or more. Contact finger is of steel spring wire, having a blunt point. Contact pressure is adjusted by compression of a coil spring at the opposite end of the contact arm. It has performed well through many heat cycles.

Figure 12 illustrates the oven, L. and N. Millivolt potentiometer, and the Millivac voltmeter as in use. Figure 13 illustrates the interior of oven, cell holder jig, etc. The asbestos sheets are used to prevent convection currents within the oven from producing a temperature differential. Light intensity is adjusted to approximately 100 Mw/cm^2 by adjustment to I_{sc} of the same value as in sunlight.

2. Comparison of Variable Gap & Single Gap Cells.

(a). Temperature characteristics.

Several single gap cells of good efficiency were selected, including one cell of 7 percent efficiency. Several variable gap cells of fairly good efficiency were also selected. Their V_{oc} , I_{sc} , Eff_{mp} at temperatures up to 175°C were checked at 25° steps. Some interesting differences were noted. Table V gives the pertinent facts on these cells with reference to V_{oc} .

TABLE V.

Comparison of Effect of Temperature on V_{oc}
in Single Gap and Variable Gap Solar Cells

Cell No.	Phosphorus Diffusion			Approx. p-n Junction Depth	V_{oc} decline/ $^\circ\text{C}$
	Eff_{mp}	Pressure	Temp. $^\circ\text{C}$		
297 V. G.	2.5%	8 atmos.	900 $^\circ\text{C}$	5 hrs.	1. Micron .00185
307 V. G.	4.6%	10 "	800 $^\circ\text{C}$	2 hrs.	1. " .00205
308 V. G.	4.2%	10 "	800 $^\circ\text{C}$	2 hrs.	1. " .00217
343 V. G.	4.6%	10 "	800 $^\circ\text{C}$	4 hrs.	1. " .00230
344 V. G.	3.8%	10 "	800 $^\circ\text{C}$	4 hrs.	1. " .00204
350 V. G.	3.3%	10 "	800 $^\circ\text{C}$	50 hrs.	1. " .00217
322 S. G.	3.9%	---	---	--	1. " .00234
348 S. G.	5.1%	---	---	--	1. " .00230
Commercial S. G. Cell,	7.6%	---	---	--	-- .00234



Figure 12. Equipment and Oven for Measuring Photo Parameters at Temperatures to 200°C.

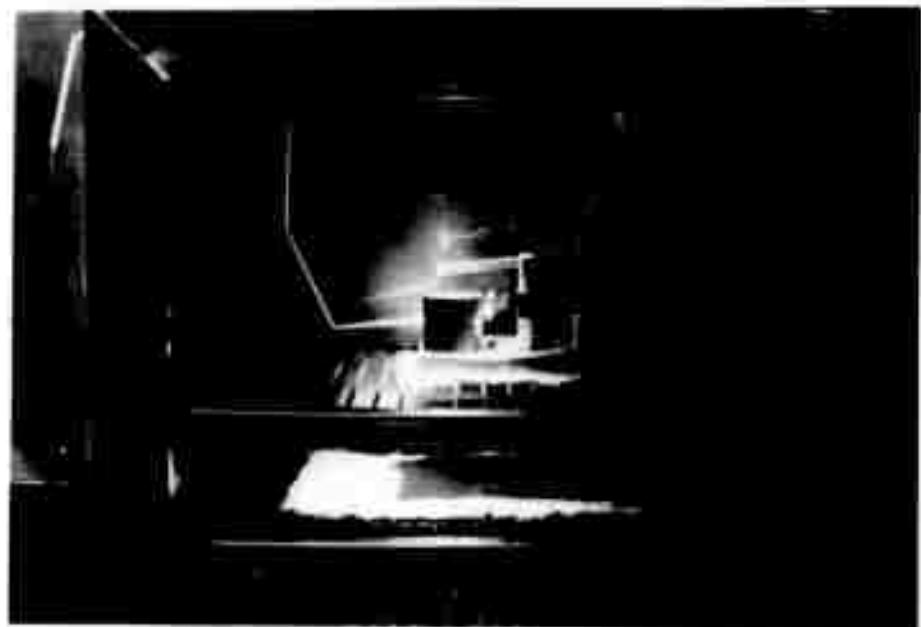


Figure 13. Interior of Oven Illustrating Cell Holder and Thermocouple.

Graphic presentation of the foregoing data is of interest as it illustrates the very linear decline in V_{oc} , thereby lending assurance to the accuracy of the measuring technique. Figure 14 illustrates typical data curves and the linear decline in V_{oc} . It is of interest that repeated measurements are in close agreement.

While the total amount of available experimental data does not yet warrant positive conclusions in the comparison of the effect of temperature on the characteristics of single gap and variable gap cells, there is indication that the decline in V_{oc} with temperature is less in the case of the variable gap cell. The data on the decline of V_{oc} with temperature in the single gap cell is very consistent giving a slope of .00234 v/ $^{\circ}$ C.

The I_{sc} change with temperature is presented in Figure 15. The same caution in conclusions must be exercised, yet the rise in I_{sc} for the variable gap cells appears to be typically steeper than for single gap cells.

It is recognized that instability of contacting and other factors could seriously affect the data observed. To our knowledge such factors did not influence the measurements.

(b). Eff_{mp} at elevated temperatures.

The Eff_{mp} of typical cells was measured between 25 $^{\circ}$ C and 175 $^{\circ}$ C.

Tentative direct comparison is presented in Table VI.

TABLE VI.

Eff_{mp} of Variable and Single Gap Cells at Elevated Temperatures.

Cell No.	Eff_{mp}	Decline Eff %/ $^{\circ}$ C 25 $^{\circ}$ C to 175 $^{\circ}$ C	Temp $^{\circ}$ C of 1/2 Room Temp. Eff_{mp}	Phosphorus Pressure $^{\circ}$ C Time
343 V.G.	4.6%	.01869	170 $^{\circ}$ C	10 Atm. 800 $^{\circ}$ C 4 hrs.
344 V.G.	3.8	.01193	185 $^{\circ}$ C	10 " 800 $^{\circ}$ C 4 hrs.
350 V.G.	3.3	.00621	230 $^{\circ}$ C	10 " 800 $^{\circ}$ C 50 hrs.
348 S.G. Commercial S.G.	5.1 7.6	.01175 .02769	175 $^{\circ}$ C 170 $^{\circ}$ C	-- --- -- -- --- --

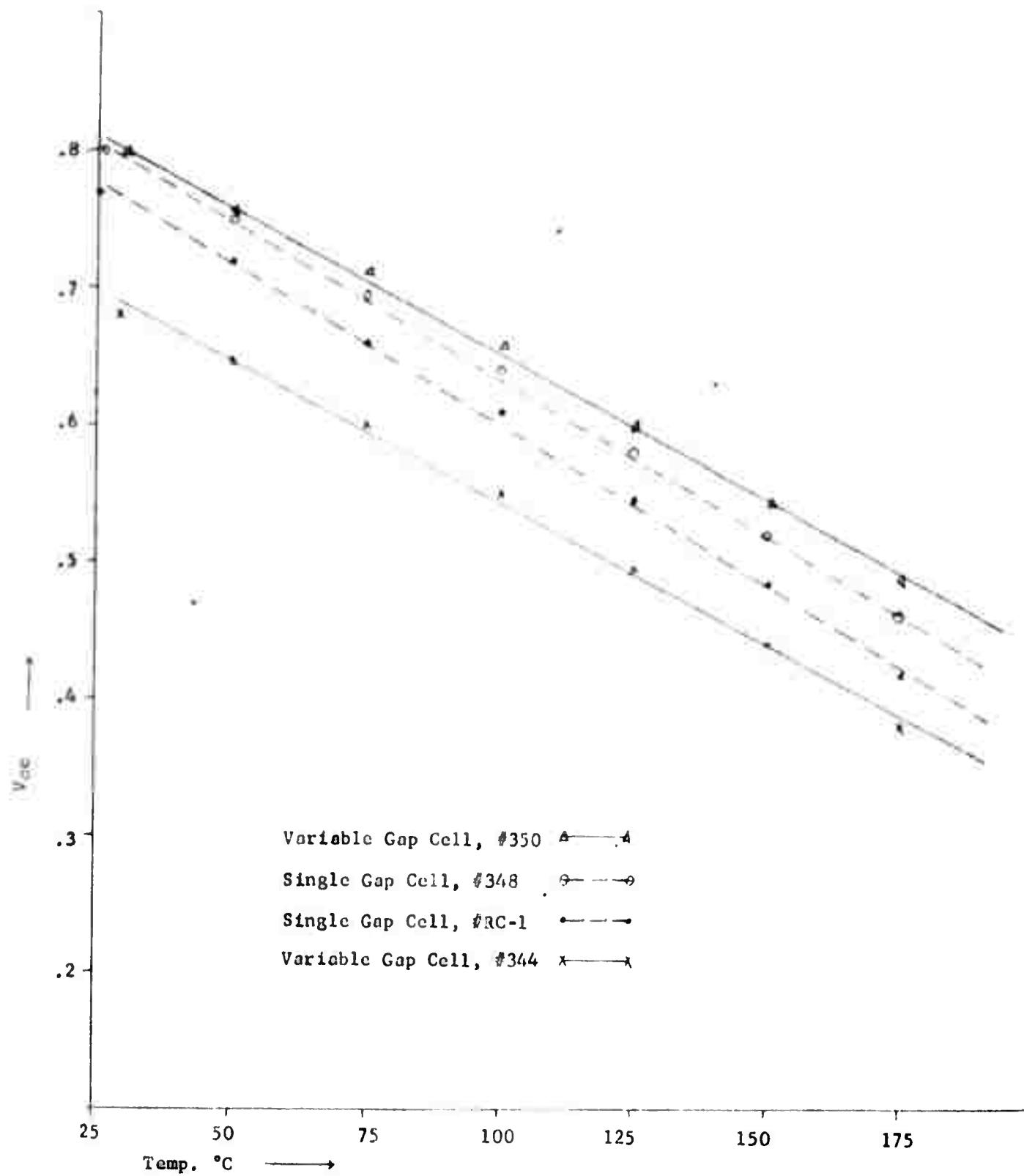


Figure 14. Decline in V_{oc} with Temperature of Variable and Single Gap Cells.

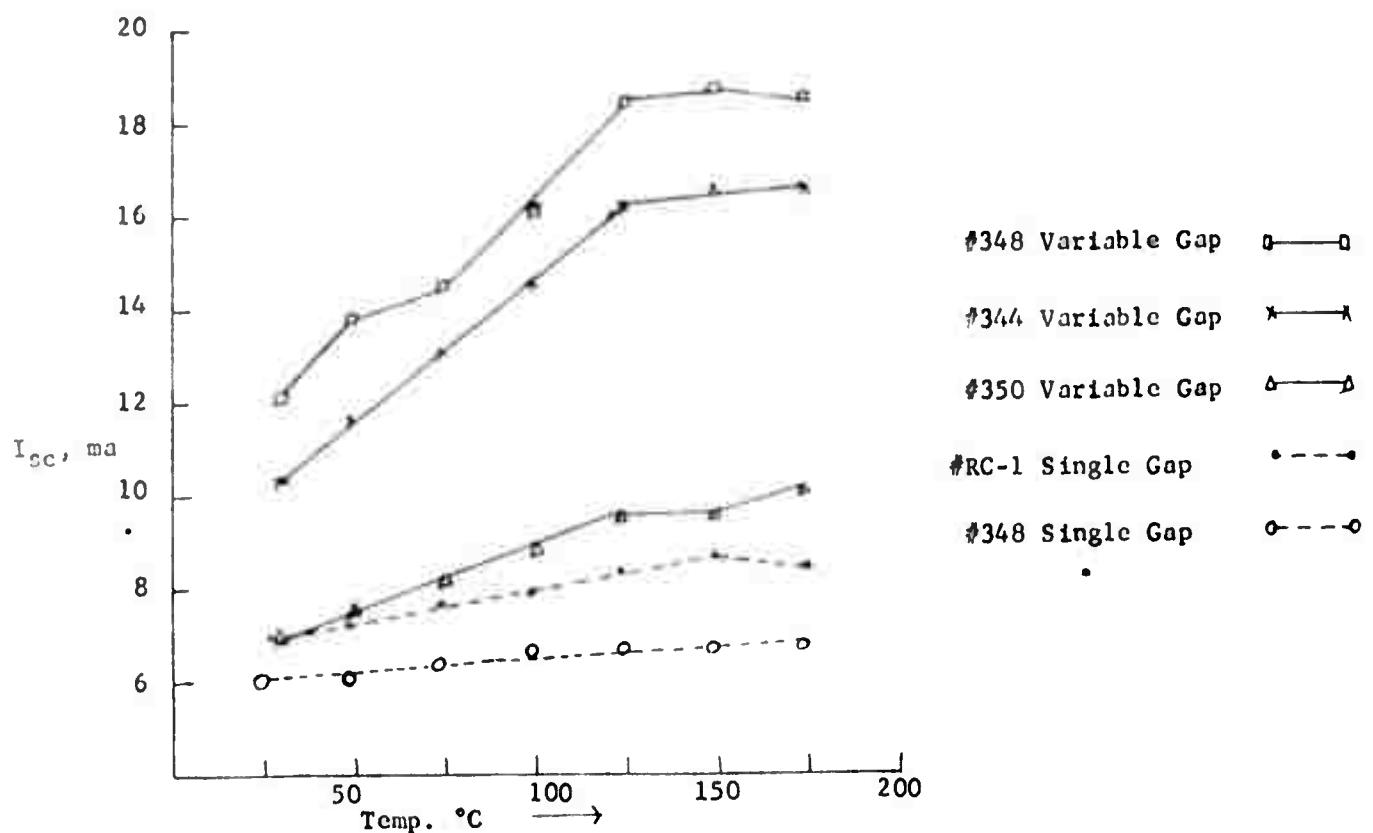
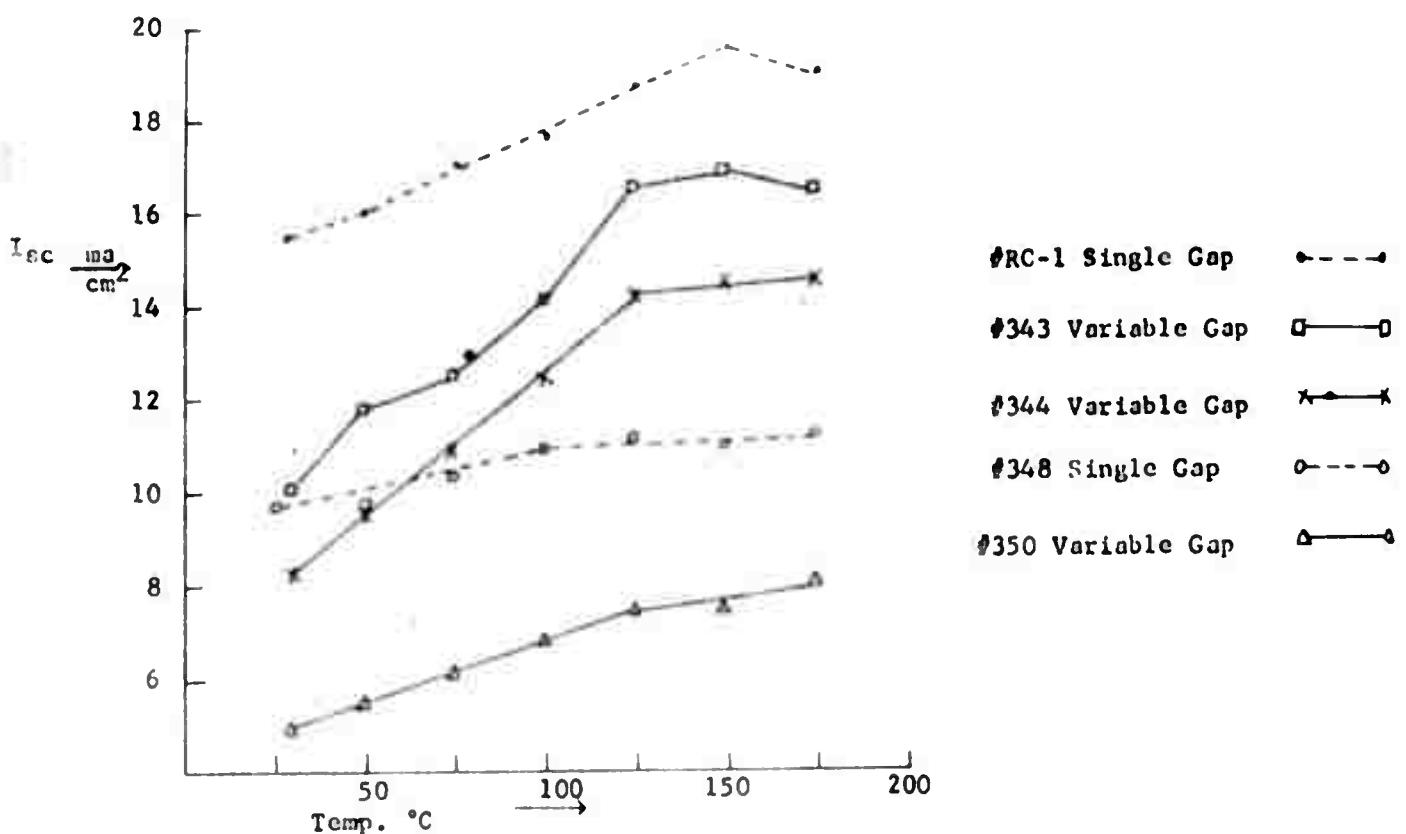


Figure 15. Change in I_{sc} of Variable and Single Gap Cells as a Function of Temperature.

No positive conclusions may yet be drawn from such a limited number of cells, with different efficiencies. Graphic presentation in Figure 16 indicates a slope more shallow for variable gap cells. This may be a reflection of either -

- (a). The effect of GaP present, or
- (b). The effect of overall cell efficiency.

(c). Spectral Response.

Spectral response, made with a Bausch & Lomb Spectrophotometer is regularly used for evaluation of junction depth and as an indication of the presence of GaP. Typically, the single gap cells indicate a peak in the region of .8 microns, the band edge of GaAs.⁽³⁾ Shallow junctions in single gap cells produce a broadening of this peak response, with some increase in response at shorter wavelengths. Typically, variable gap cells indicate increased response in the region of .6 microns, and a slight shift of the peak response toward the short wavelength region. Figure 17 depicts this characteristic difference between #305 variable gap cell and a single gap gallium arsenide cell (6.1% conversion efficiency).

(d). Diode Characteristics.

Diode characteristics are routinely monitored using a Tektronix Oscilloscope Type 535, and diode curve tracer adapter. Data thus obtained has produced improvement in lowering contact resistance, in assuring ohmicity of contacts for resistivity measurement, etc.

Typical diode characteristics of single gap cells and variable gap cells are illustrated in Figure 18. It will be noted that in variable gap cells of good efficiency the forward characteristics closely approximate those of single gap cells while a somewhat higher inverse voltage appears characteristic in the variable gap cells.

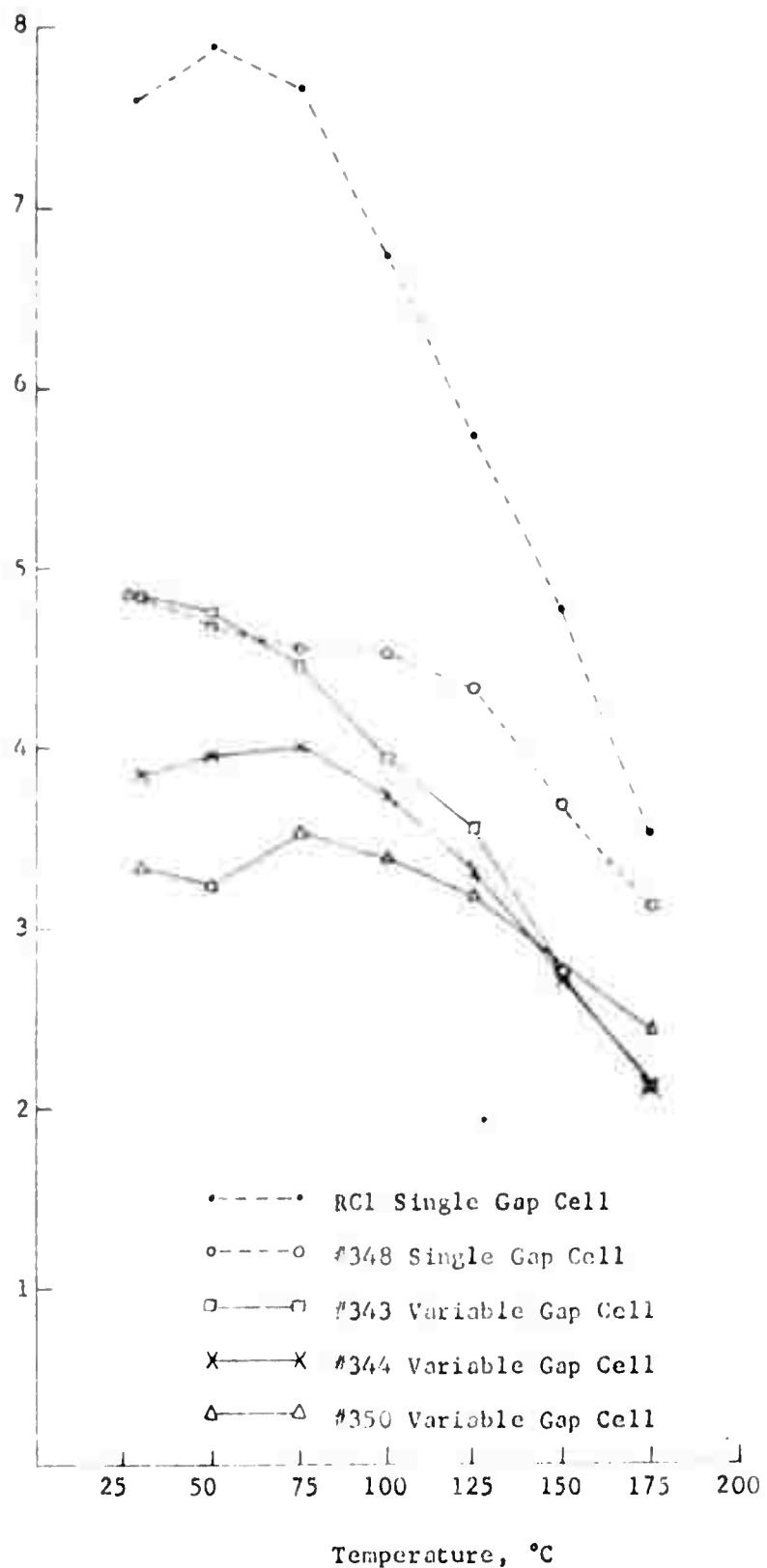


Figure 16. Efficiency of Variable and Single Gap Cells as a Function of Temperature.

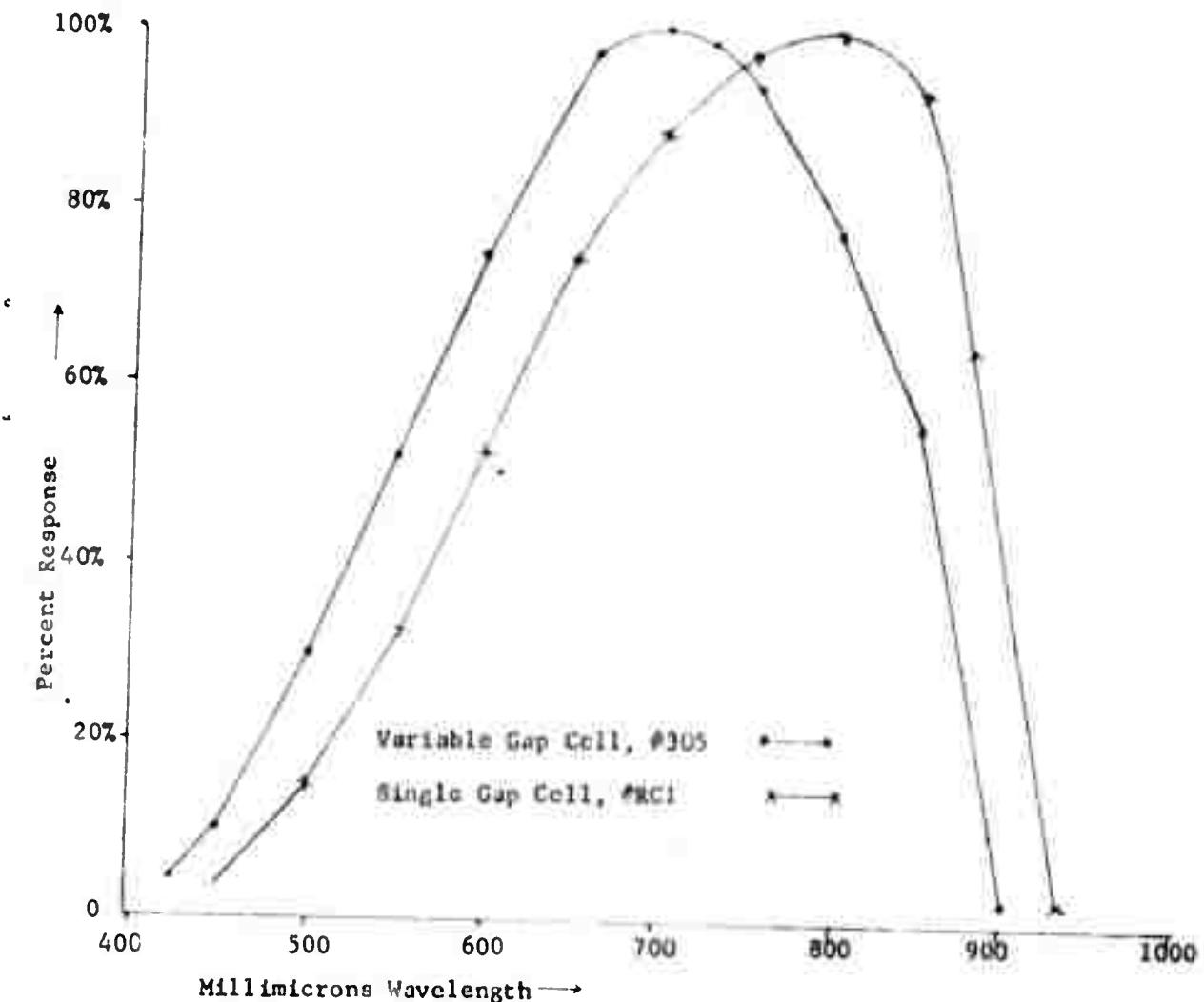


Figure 17. Comparison of Spectral Response of Variable Gap and Single Gap Cells.

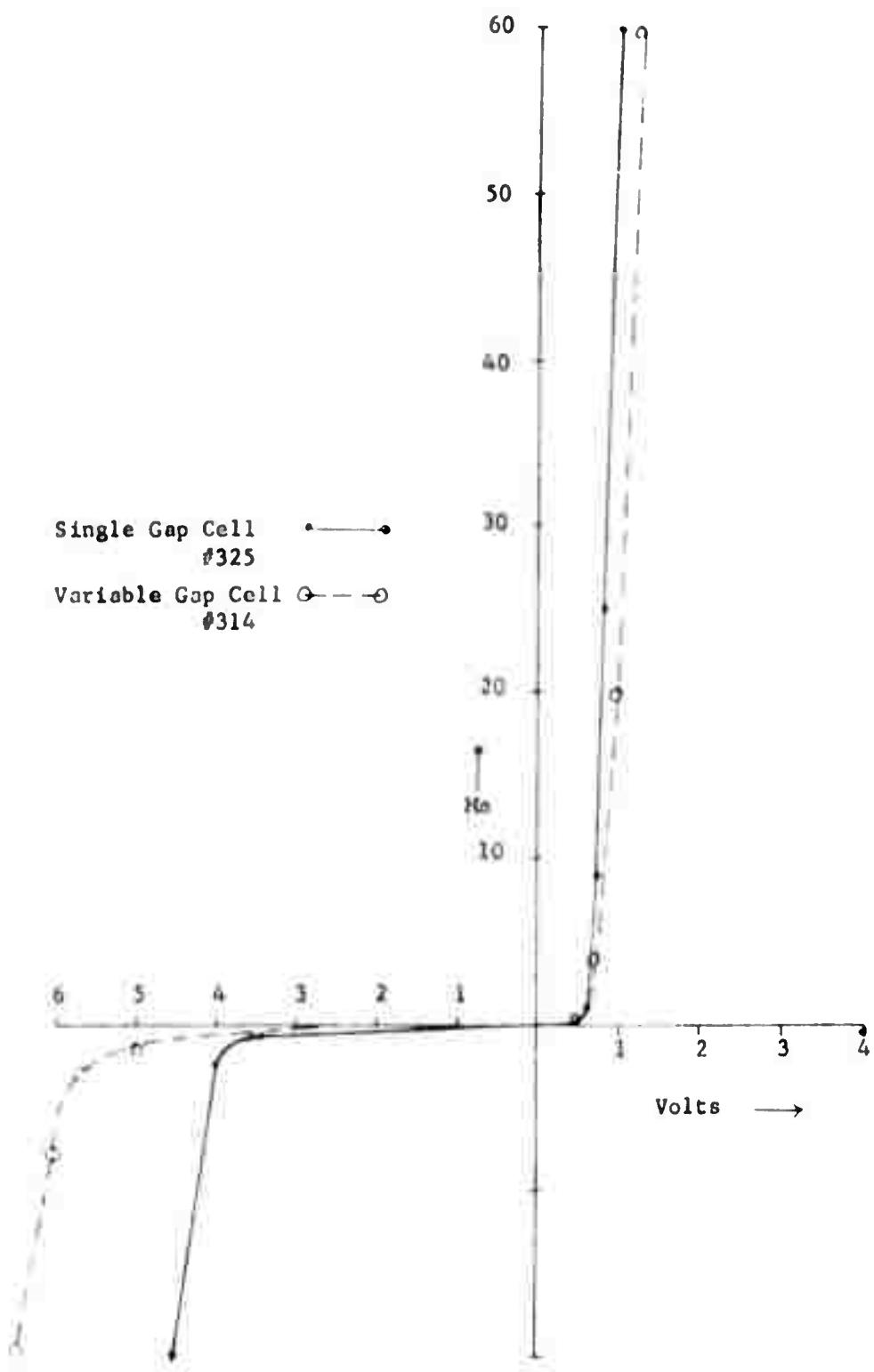


Figure 18. Diode Characteristics of Typical Variable Gap and Single Gap Cells.

A definite peculiarity was noted in the dark diode characteristic of all of the cells made from two particular lots of Czochralski and float-zoned gallium arsenide single crystal material. All of the material of these two lots was of approximately the same resistivity (.05 ohm-cm), mobility, and carrier concentration. This characteristic was manifested by the extremely high forward voltage required to obtain appreciable current flow, and the very sharp break in reverse current. The characteristic, somewhat similar to Zener diode behavior is illustrated in Figure 19. It is believed to be characteristic of this particular material, since cells made from Czochralski crystals, gradient freeze crystals, and float zoned material from different lots, having approximately the same resistivity and mobility had normal diode characteristics. It is considered that (1) contacting was definitely not the cause of the difference in the cells, and (2) there was inherent differences in the material - possibly due to some differences in crystalline structure brought about by variation in the rate of freezing.

(e). Carrier Concentration and Junction Depths.

Carrier concentrations are determined by 4-probe resistivity measurements, based on 1-micron junctions in most cases. Values generally are of the order of 10^{19} atms/cm² in both variable and single gap cells.

Junction depth in single gap cells is measured by an etching-weight loss method.⁽⁴⁾ This technique provides an indication also of the doping gradient at the junction. Depths in variable gap cells have not proved amenable to measurement by this method. A good etchant for this purpose is needed, and continued effort along this line will be made. The depth is estimated on the basis that the effective diffusion constant of zinc in GaP is high as reported.⁽⁵⁾ Quench cooling of the

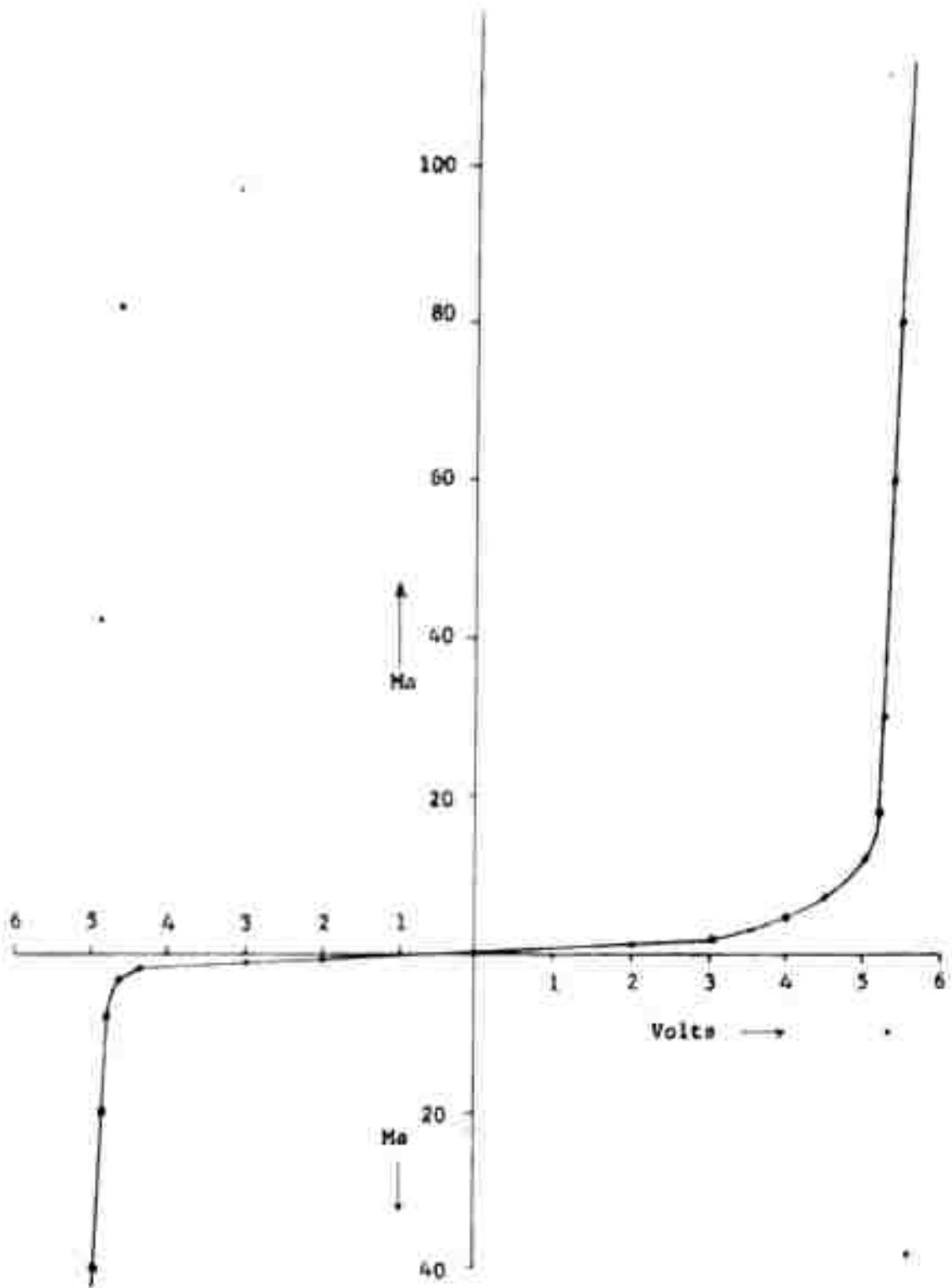


Figure 19. Diode Characteristics Observed Related to Starting Material.

diffused junction is done to avoid anneal-precipitation centers in the GaP layer. (5)

V. CONCLUSIONS

The results of the investigation thus far indicate:

1. That GaP as a discrete single phase is produced by the diffusion technique and by indirect methods the approximate depth-concentration can be determined.
2. The data indicates a definite advantage of the variable gap cells in elevated temperature characteristics, particularly in I_{sc} change. Further improvement may reasonably be expected with cells where the junction lies in a region of high GaP content rather than below it.
3. Considerable improvement in Eff_{mp} and reproducibility in both variable gap and single gap cells has been achieved without the use of etching as an integral step in fabrication.
4. Simple and effective zinc diffusion by the open tube hydrogen technique has offered excellent junction depth control and expedites cell fabrication.
5. Refinement in technique, gas purification and material, enabling an increase in variable gap efficiencies should emphasize the better temperature parameters of the cells.
6. Reliable and ohmic contacts to "p" type GaAs can be produced by the sputtering of platinum and coating with either solder or baked on silver paste.
7. Non-uniformity in starting material can have a serious influence on diode characteristics and therefore on cell efficiencies. This non-homogeneous factor may be more likely in rapidly crystallized material, such as in Czochralski or float-zoned material.

VI. FUTURE STUDIES

It is proposed that future studies should include:

- (A). Continued effort to determine the lowest temperature, lowest phosphorus pressure, and shortest time required to produce a homogeneous layer of GaP, of approximately 1-micron depth on the surface of GaAs wafers.
- (B). Investigation of the feasibility of epitaxially "growing" GaP on the surface of GaAs wafers.
- (C). Continued effort in obtaining a suitable etchant or solvent for GaP to facilitate junction depth measurement, cleaning of surface, and proving the "window" effect of the higher band gap material as discussed below.
- (D). A study, involving the use of integrated red light to monitor the rate of increase of response to such light of a cell whose surface is removed (preferably chemically). Such a cell would have it's junction lying below the GaP layer, in the upper region of GaAs. The "window" effect should indicate little increase in response as the GaP is removed, and rapid increase as the uppermost GaAs was removed.

Such a study has been started, a light source and filter suitable for use is illustrated in Figure 20.

- (E). Continued emphasis on the evaluation of temperature parameters of the variable gap cells. It is considered this will be productive, especially as the technique of forming the GaP layer is improved.



Figure 20. Integrated Red Light Source.

The lamphouse contains a 150-watt incandescent bulb. The aluminum middle section houses condensing and collimating lenses and a variable aperture. The bottom section with the black band at its center contains a Corning Glass filter, Type CS2-64 passing wavelength longer than .64 microns, and is movable vertically a distance of 2 inches. This allows the end to be inserted in a simple light shield for the cell holder. The light shield (not shown) is of cardboard, with a hole in its top closely matching the diameter of the filter barrel.

(F). Evaluation and comparison of dark diode characteristics of variable gap and single gap cells as a function of temperature as corroborative evidence of the improved temperature characteristics of the variable gap cell.

(G). Continued concurrent accumulation of data to enable specification of best resistivity, mobility, lifetime, and growth type of material to obtain maximum efficiencies in variable gap solar cells.

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C.J. Frosch, and R.M.Mikulyak.

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Accession No.	Classification	Information
AB	UNCLASSIFIED	<p>1. Solar Energy Converters, Photovoltaic 2. Variable Gap Solar Cells 3. Temperature Effect on Photo-voltaic Cells.</p> <p>The Kola-Pitcher Company, Chemical & Metals Division, Miami, Oklahoma. INVESTIGATION OF DIFFERENTIALLY CONDUCTING VARIABLE GAP PHOTOVOLTAIC SOLAR ENERGY CONVERTERS.</p> <p>L. E. Stoen and W. F. McNeill First Semimonthly Technical Report - Feb. 9, 1961 to June 30, 1961. 111 pp. - Illus. - Graphs. Signal Corps Contract No. DA-36-0795-SC-37674 (Subcontract Report).</p> <p>Gallium phosphide on a discrete sheet was subjected to the diffusion of gallium arsenide powder at 1100°C. under a hydrogen atmosphere. The pressure of 20 atmospheres resulted in the formation of a discrete phase of gallium phosphide. Distribution of discrete phase was determined by x-ray diffraction. Concentration of discrete phase due to the diffusion treatment was determined by x-ray analysis to be 82.3 percent with GaAs concentration of 17.7 percent. An advantage of variable gap solar cells can be obtained by using gallium arsenide powder to produce a discrete phase. GaAs cells are simple, inexpensive to fabricate and have a temperature characteristic similar to silicon cells. Their difference in the open circuit voltage is due to the difference of their band gaps. Since the open circuit voltage is dependent over the entire emission distribution, Reilach demonstrated that p^- type GaAs can be produced by sputtering with pressure filaments by coating with molten tin. Working on silicon, he indicated that non-homogeneity in gallium arsenide single crystal can have a serious negative influence on diode characteristics and conversion efficiency of solar cells under illumination.</p>
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